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(54) Title: HYDROGEN SULFIDE-CARBON DIOXIDE MEMBRANE SEPARATION PROCESS USING PERFLUORINATED MEMBRANES

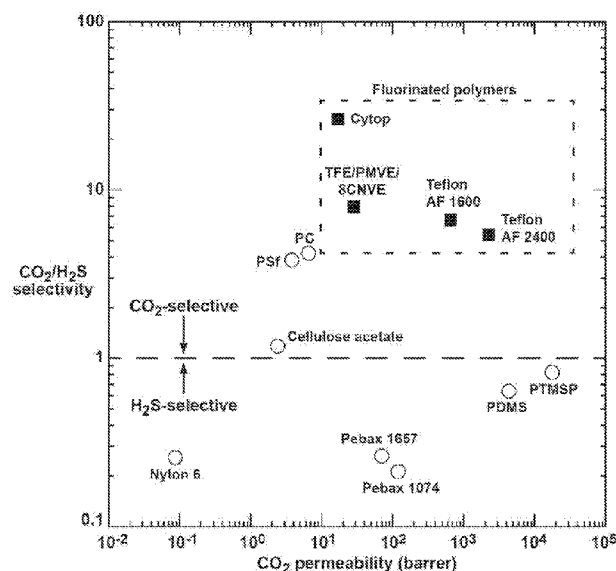


FIG. 2

(57) **Abstract:** A process for recovering sulfur from a sour gas is provided. The process includes the steps of: providing the sour gas to a membrane separation unit having a carbon dioxide-selective membrane that comprises a perfluoropolymer, wherein the sour gas comprises carbon dioxide and at least 1 mol % hydrogen sulfide; separating the sour gas using the carbon dioxide-selective membrane in the membrane separation stage to obtain hydrogen sulfide-enriched gas and hydrogen sulfide-stripped gas, wherein the hydrogen sulfide-enriched gas has a hydrogen sulfide concentration of at least 20 mol %, and wherein the hydrogen sulfide-stripped gas comprises carbon dioxide; and processing the hydrogen sulfide-enriched gas in a sulfur recovery unit to obtain sulfur.



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HYDROGEN SULFIDE-CARBON DIOXIDE MEMBRANE SEPARATION PROCESS USING PERFLUORINATED MEMBRANES

TECHNICAL FIELD

[0001] This disclosure generally relates to membrane separation processes and systems for enriching hydrogen sulfide in sour gas streams for processing in a sulfur recovery complex.

BACKGROUND OF THE ART

[0002] Hydrogen sulfide is a reactive and poisonous contaminant that is sometimes found in industrial processes and process streams involving hydrocarbons. Hydrogen sulfide in industrial process streams can be converted to elemental sulfur in a sulfur recovery complex, which may include processing hydrogen sulfide-rich gas in a Claus unit. In a Claus unit, hydrogen sulfide is first partially oxidized to produce sulfur dioxide and then reacted in the presence of a catalyst to produce elemental sulfur and water vapor. By maintaining a sufficiently high temperature in the oxidation stage of the Claus unit, other contaminants present in the hydrogen sulfide-rich gas (e.g., mercaptans, carbonyl sulfide, carbon disulfide, benzene, toluene, and xylene) can be eliminated.

[0003] When hydrogen sulfide concentrations are sufficiently high, the energy released in the oxidation of hydrogen sulfide is sufficient to carry out the partial oxidation of hydrogen sulfide and to eliminate other contaminants. But additional energy must be provided when hydrogen sulfide concentrations are too low. Naturally, the presence of other compounds (e.g., carbon dioxide) in the sour gas can reduce the concentration of hydrogen sulfide in the sour gas. Amine absorption processes are used conventionally to remove carbon dioxide and enrich hydrogen sulfide in a sour gas before introducing it to the sulfur recovery complex. However, conventional amine absorption processes are costly and limited in their ability to produce enriched hydrogen sulfide.

[0004] There is a need for more cost-effective hydrogen sulfide enriching processes capable of reliably producing higher concentrations of hydrogen sulfide.

SUMMARY

[0005] A general object of this disclosure is to provide systems and processes for enriching hydrogen sulfide in a sour gas for processing in a sulfur recovery complex. The systems and processes disclosed here involve removing carbon dioxide from a sour gas using a membrane separation unit to enrich hydrogen sulfide in the sour gas, and delivering hydrogen sulfide-enriched gas to a sulfur recovery complex for the production of sulfur.

[0006] A process for recovering sulfur from a sour gas is provided. The process includes the steps of: providing the sour gas to a membrane separation unit having a carbon dioxide-selective membrane that comprises a perfluoropolymer, wherein the sour gas includes carbon dioxide and at least 1 mol % hydrogen sulfide; separating the sour gas using the carbon dioxide-selective membrane in the membrane separation stage to obtain hydrogen sulfide-enriched gas and hydrogen sulfide-stripped gas, wherein the hydrogen sulfide-enriched gas has a hydrogen sulfide concentration of at least 20 mol %, and wherein the hydrogen sulfide-stripped gas includes carbon dioxide; and processing the hydrogen sulfide-enriched gas in a sulfur recovery unit to obtain sulfur.

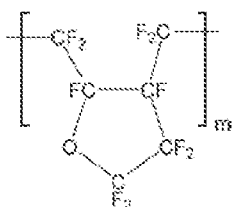
[0007] According to at least one embodiment, the hydrogen sulfide-stripped gas also contains residual hydrogen sulfide, and the process also includes the steps of: oxidizing the hydrogen sulfide-stripped gas in an oxidizer such that the residual hydrogen sulfide in the hydrogen sulfide-stripped gas is reacted with oxygen to produce sulfur dioxide-bearing gas. The sulfur dioxide-bearing gas can be vented to the atmosphere, or captured for use in enhanced oil recovery operations.

[0008] According to at least one embodiment, the sulfur dioxide-bearing gas can have a concentration of hydrogen sulfide that is less than 0.1 mol %, alternately less than 0.015 mol %, alternately less than 0.01 mol %. The hydrogen sulfide enriched gas can have a concentration of hydrogen sulfide that is greater than 80 mol %, alternately greater than 90 mol %, alternately greater than 95 mol %.

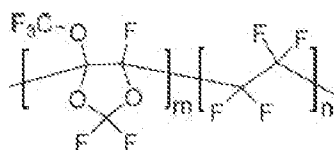
[0009] According to at least one embodiment, the carbon dioxide-selective membrane can have carbon dioxide-hydrogen sulfide selectivity greater than 10, alternately greater than 20, alternately greater than 30.

[00010] According to at least one embodiment, the membrane separation unit can have a single-pass membrane stage configuration. According to at least one embodiment, the membrane separation unit can have a two-stage retentate-in-series membrane configuration. According to at least one embodiment, the membrane separation unit can have a two-stage permeate-in-series membrane configuration. According to at least one embodiment, the membrane separation unit can have a three-stage membrane configuration.

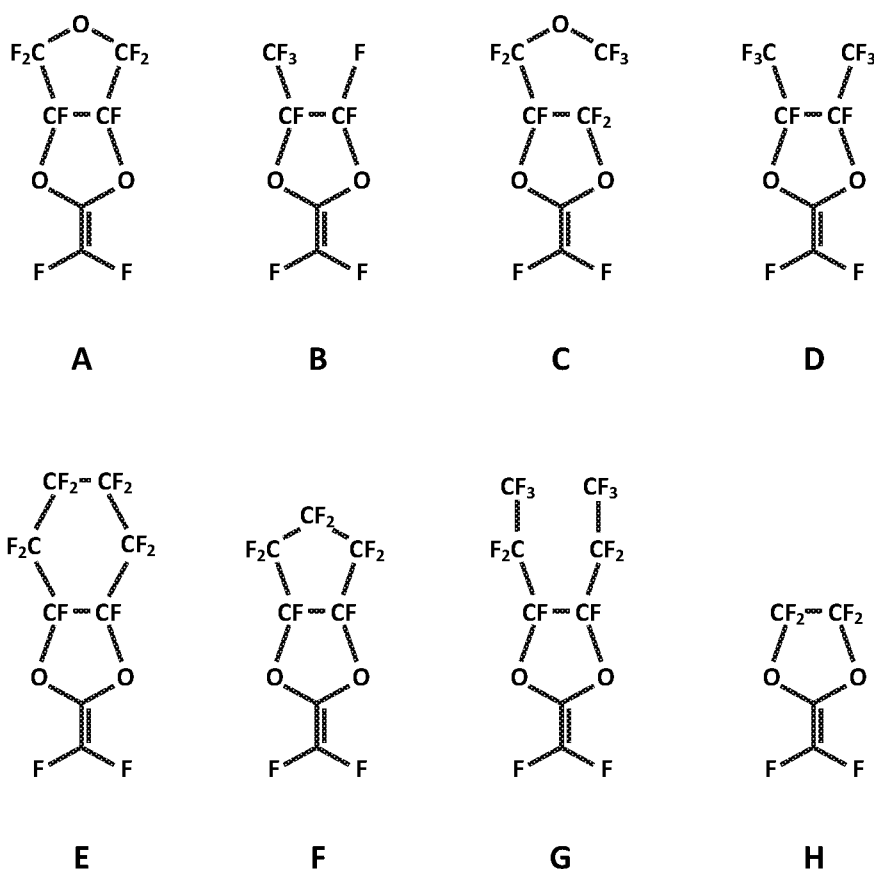
[00011] According to at least one embodiment, the perfluoropolymer can include a monomer having the following chemical structure:



[00012] According to at least one embodiment, the perfluoropolymer can include a monomer having the following chemical structure:



[00013] According to at least one embodiment, the perfluoropolymer can include a monomer having a chemical structure selected from the group consisting of:



BRIEF DESCRIPTION OF THE DRAWINGS

[00014] The embodiments disclosed here will be understood by the following detailed description along with the accompanying drawing. The embodiment in the figure is given as an example; the disclosure is not limited to the content of the illustration.

[00015] **Fig. 1** is a plot showing hydrogen sulfide-carbon dioxide separation using a selective amine absorption process.

[00016] **Fig. 2** is a plot showing carbon dioxide-hydrogen sulfide selectivity for various membranes as a function of carbon dioxide permeability.

[00017] **Fig. 3** shows structural formulas for some perfluoropolymer monomers useful for making homopolymers and copolymers, which are particularly useful in the membranes of some embodiments.

[00018] **Fig. 4** is an illustration of various process diagrams of membrane separation processes for separating carbon dioxide and hydrogen sulfide: **Fig. 4a** is a process diagram of

a single-pass membrane separation process; **Fig. 4b** is a process diagram of a two-stage retentate-in-series membrane separation process; **Fig. 4c** is a process diagram of a two-stage permeate-in-series membrane separation process; **Fig. 4d** is a process diagram of a three-stage membrane separation process.

DETAILED DESCRIPTION

[00019] This disclosure describes various embodiments related to systems and methods for enriching hydrogen sulfide in a sour gas for feed to a sulfur recovery unit. For certain embodiments, many details are provided for thorough understanding of the various components or steps. In other instances, well-known processes, devices, compositions, and systems are not described in particular detail so that the embodiments are not obscured by detail. Likewise, illustrations of the various embodiments can omit certain features or details so that various embodiments are not obscured.

[00020] The drawings provide illustrations of various embodiments. Other embodiments can be used, and logical changes can be made without departing from the scope of this disclosure. The following detailed description and the embodiments it describes are not to be considered limiting. Many other undisclosed changes and modifications to the embodiments disclosed in this disclosure can fall within its scope. The patentable scope is defined by the claims, and can include other examples that occur to those skilled in the art. The scope of the claims includes other examples that may have equivalent elements to those described in the claims.

[00021] As used in this disclosure, the term “hydrogen sulfide” is used synonymously with the terms “dihydrogen sulfide” and “dihydrogen monosulfide” and has the chemical formula H_2S .

[00022] As used in this disclosure, the term “carbon dioxide” has the chemical formula CO_2 .

[00023] Sour gas streams intended for sulfur recovery sometimes contain a lower concentration of hydrogen sulfide than is suitable for processing in a sulfur recovery unit. And even in instances where the sour gas contains a suitable concentration of hydrogen sulfide for processing in a sulfur recovery unit, it may be desirable to enrich the gas in hydrogen sulfide further to improve the performance of the sulfur recovery unit. Typically, the sulfur recovery process is carried out using a Claus plant. Gases fed to the Claus plant must contain at least 20 mol % hydrogen sulfide. Preferably the feed gas contains at least 50 mol % hydrogen

sulfide, more preferably at least 80 mol %, most preferably at least 90 mol %. A higher concentration of hydrogen sulfide in gases fed to a Claus plant generally results in a higher temperature in the Claus plant furnace; which in turn results in less supplemental fuel being used and the destruction of contaminants such as aromatics, ammonia (NH₃), carbon monoxide (CO), carbonyl sulfide (COS), carbon disulfide (CS₂), and thiols (R-SH).

[00024] An example of a sour gas can be hydrogen sulfide-containing natural gas or a hydrogen sulfide-containing gas obtained from natural gas. Much of the world's natural gas supply contains more than 2 mol % carbon dioxide and more than 4 ppm hydrogen sulfide. Before natural gas containing such concentrations of carbon dioxide and hydrogen sulfide can be used or delivered to a pipeline, it is usually treated to bring concentrations of carbon dioxide and hydrogen sulfide down to suitable levels. The carbon dioxide and hydrogen sulfide removed from the natural gas can be used in a sulfur recovery process as described in this disclosure.

[00025] Another example of a sour gas is a hydrogen sulfide-containing gas produced in the treatment of sulfur-containing oil in a refinery process. Oil products usually must be treated to reduce sulfur content to very low concentrations. Sulfur-containing oil is often treated by reacting the sulfur in the oil with hydrogen to obtain hydrogen sulfide along with some light hydrocarbons. These gases are usually treated using nonselective amine absorption to obtain a concentrated hydrogen sulfide stream. For some processes, the sour gas obtained is suitable for processing in a sulfur recovery unit without further enrichment. However, some processes produce a sour gas stream that contains a substantial amount of carbon dioxide and a relatively dilute concentration of hydrogen sulfide. For example, a refinery process can produce a sour gas stream that contains between about 1 and 50 mol % hydrogen sulfide, alternately between about 1 and 10 mol %, alternately between about 10 and 40 mol %, alternately between about 5 and 15 mol %. It is desirable to enrich hydrogen sulfide in such streams before they are sent to a sulfur recovery unit.

[00026] Other sources of sour gas can include syngas from the gasification of coal, biomass, or municipal waste. Such streams can contain a variety of concentrations of hydrogen sulfide. By way of example, syngas produced by the gasification of coal usually contains a mixture of carbon monoxide, hydrogen, and carbon dioxide, and can contain between about 0.3–3 mol % hydrogen sulfide. Typically, this stream must be treated to reduce the concentration of carbon dioxide and hydrogen sulfide before it can be used to make chemicals.

[00027] Amine absorption processes are commonly used to concentrate hydrogen sulfide in gases fed to sulfur recovery units. Such processes require large absorption and stripping columns, and can be costly to operate. Moreover, such processes have a limited capacity for achieving high concentrations of hydrogen sulfide. The processes and systems described in this disclosure can be used to reduce the size of, or eliminate completely, an amine absorption unit for concentrating hydrogen sulfide in gases fed to a sulfur recovery unit.

[00028] This disclosure discusses nonselective absorption processes and selective absorption processes. Nonselective absorption processes are typically used to separate hydrogen sulfide and carbon dioxide from a feed stream such as syngas to produce a product stream suitable for use downstream. Selective absorption processes are configured to preferentially remove most or all of a particular acid gas component (such as hydrogen sulfide), and may remove only a portion of another acid gas component (such as carbon dioxide).

[00029] A liquid solvent for selectively removing acid gas components (e.g., hydrogen sulfide, carbon dioxide, carbonyl sulfide, etc.) from syngas can be used in an absorption process to remove hydrogen sulfide, carbon dioxide, and other contaminants. The efficiency of the process will be determined by certain absorption characteristics of the solvent. Absorption can be a simple physical solution of the gases or it can involve a reversible chemical reaction between the specific gases and some components of the solvent mixture.

[00030] Suitable physical solvents for carbon dioxide separation include methanol at temperatures between -20 and -30 °C (the Rectisol[®] process), dimethyl ethers of polyethylene glycol, DMPEG (the Selexol[®] process), and n-methyl-2-pyrrolidone (NMP; the Purisol[®] process). Suitable chemical solvents include aqueous amine solutions of mono- and diethanolamine (MEA; DEA), methyl diethanolamine (MDEA), and diisopropanolamine (DIPA). Methyl diethanolamine is the most commonly used chemical solvent.

[00031] Chemical absorption is suitable for removing carbon dioxide from a carbon dioxide-containing gas if the concentration of carbon dioxide in the gas is relatively low (i.e., less than about 15 mol %) and at moderate pressure (i.e., between about 10–30 bar). However, physical absorption may be preferred if the carbon dioxide-containing gas has a concentration of carbon dioxide that is greater than about 15 mol % or pressure that is greater than about 30 bar. For example, physical absorption processes such as Rectisol[®], Selexol[®], or Purisol[®] may be

preferable for a gas with a concentration of carbon dioxide greater than about 20 mol % or a pressure greater than about 40 bar.

[00032] Some nonselective amine absorption processes can use MEA to remove carbon dioxide and hydrogen sulfide to produce a product gas containing between about 1 and 2 mol % carbon dioxide and less than about 1 ppm hydrogen sulfide. The acid gases removed are typically collected in a stream with a concentration of hydrogen sulfide that varies widely. In some instances, the concentration of hydrogen sulfide in the stream is sufficiently high to be sent directly to a sulfur recovery unit. However, it is common for the stream to be treated to enrich hydrogen sulfide for the sulfur recovery process.

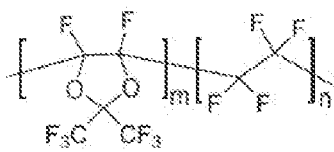
[00033] An example of a selective amine absorption process involves using MDEA to selectively separate hydrogen sulfide from a stream containing both hydrogen sulfide and carbon dioxide. Figure 1 shows a plot of hydrogen sulfide concentration in a recovered hydrogen sulfide-enriched gas from a selective amine absorption process as a function of concentration of hydrogen sulfide in the feed gas to the process. In such a process, the MDEA selectively absorbs nearly all of the hydrogen sulfide in the feed gas along with a portion of the carbon dioxide in the feed gas. Because a portion of the carbon dioxide is also absorbed, the process results in only partial enrichment of hydrogen sulfide. The concentration of hydrogen sulfide in the stripped feed gas will typically be less than 20–50 ppm, or less than between 50–100 ppm. In some instances, the stripped feed stream can be catalytically or thermally oxidized and then safely released to the atmosphere without additional treatment. As shown in Fig. 1, the amine absorption process is most effective at treating a feed gas having a relatively low concentration (i.e., less than about 20 mol %) of hydrogen sulfide. For streams having a greater concentration of hydrogen sulfide, the effectiveness of the process is rather marginal.

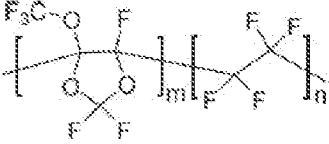
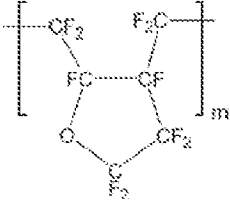
[00034] In industrial processes, gas streams containing hydrogen sulfide can be treated in a membrane separation unit to obtain hydrogen sulfide-rich gas for feed to a sulfur recovery complex. The membrane separation unit can have a membrane separation stage that includes a carbon dioxide-selective membrane, where carbon dioxide is the fast (i.e., more permeable) gas. A desirable gas membrane has high selectivity (i.e., separating power) and high permeability to the fast gas. Factors affecting carbon dioxide-hydrogen sulfide selectivity are described in a paper by TC Merkel and LG Toy, “Comparison of hydrogen sulfide transport properties in fluorinated and nonfluorinated polymers,” *Macromolecules*, 2006, 39(22), 7591–7600. Some of the data available in that paper is reproduced in Fig. 2, which shows membrane

permeability and selectivity for carbon dioxide for various membrane materials. In some embodiments, the carbon dioxide-selective membrane comprises perfluorinated polymer compounds, which can have minimum carbon dioxide-hydrogen sulfide selectivity in the range of about 5–30. According to at least one embodiment, the carbon dioxide-selective membrane has selectivity of at least about 5, alternately at least about 10, alternately at least about 20, alternately at least about 30.

[00035] Because perfluoropolymers are relatively insoluble, it is difficult to produce thin membranes using conventional solution casting and coating methods. Only three amorphous solvent-processable glassy perfluoropolymers are commercially available presently, which are identified using the trade names Teflon[®] AF (DuPont[™]), Cytop[®] (Asahi Glass[™]), and Hyflon[®] AD (Solvay[™]). These perfluoropolymers can be described as either copolymers of perfluorodioxole rings and tetrafluoroethylene (Teflon[®] AF and Hyflon[®] AD) or a cyclic perfluoro homopolymers (Cytop[®]). The dioxole rings of these polymers generally hinder polymer chain packing, resulting in amorphous polymers with relatively high gas permeability. When tetrafluoroethylene is used with the copolymers to improve processability, the gas permeability is also lowered and size selectivity is increased in Teflon[®] AF and Hyflon[®] AD. There is a difference of two orders of magnitude between the most nitrogen-permeable polymer (Teflon[®] AF2400) and the least nitrogen-permeable polymer (Cytop[®]) (Table 1). These perfluoropolymers are much more permeable than conventional glassy polymers used for membrane gas separations, but they also have reduced size selectivity.

TABLE 1 Properties of commercially available amorphous glassy perfluoropolymers suitable for solvent processing

Polymer	Chemical structure	Glass transition temperature (°C)	Nitrogen permeability (barrer) ^a	O ₂ /N ₂ selectivity
Teflon [®] AF2400		240	480	2.0

Hyflon® AD60		134	24	2.9
Cytop®		108	5.0	3.3
a	Barrer = 3.348×10^{-19} kmol/m · s · Pa			

[00036] A new class of amorphous perfluoropolymers has been developed by Membrane Technology and Research, Inc. using the perfluoro monomers shown in Fig. 2. Two of these monomers are particularly useful: perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane (Monomer D), and perfluoro-2-methylene-1,3-dioxolane (Monomer H). Characterization and synthesis of these perfluoropolymers have been described by Okamoto et al., “Synthesis and properties of amorphous perfluorinated polymers,” *Chimica oggi/Chem. Today*, 27(4), pp. 46–48; Koike et al., “Synthesis and radical polymerization of perfluoro-2-methylene-1,3-dioxolanes,” *Macromolecules*, 38, no. 23 (2005), pp. 9466–9473; Koike et al., “Synthesis and characterization of copolymers of perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) and perfluoro(2-methylene-1,3-dioxolane),” *J. Fluor. Chem.*, 156 (2013), pp. 198–202; Mikeš et al., “Characterization and properties of semi crystalline and amorphous perfluoropolymers: poly(per-fluoro-2-methylene-1,3-dioxolane),” *Polym. Adv. Tech.*, 22 (2011), pp. 1272–1277.

[00037] The monomers and chemical structures shown in Fig. 3 are preferred for use in the carbon dioxide-hydrogen sulfide selective membranes of this disclosure. Of these, homopolymers and copolymers made from Monomer B, Monomer D, and Monomer H are particularly preferred. Copolymerization of these monomers can be carried out in bulk and in hexafluorobenzene solution using perfluoro dibenzoyl peroxide. Because monomer reactivity ratios are nearly equal, resulting copolymers form an ideal random structure. For example, if the composition of Monomer D is greater than about 30 mol % the resulting copolymers are completely amorphous and soluble in fluorinated solvents. Typical glass transition temperature (T_g) results are shown in Table 2.

TABLE 2 Glass transition temperature (T_g) resulting from various copolymer compositions of Monomer D and Monomer H

Polymer	Monomer D composition (mol %)	Monomer H composition (mol %)	T_g (°C)
Monomer D	100	0	165
Copolymer 1	74	26	155
Copolymer 2	58	42	145
Copolymer 3	43	57	125
Copolymer 4	20	80	106
Monomer H	0	100	228 ^a

^a Melting temperature (T_m).

[00038] Copolymers of Monomer D and Monomer H can achieve combinations of selectivity and permeance that are unattainable using commercially available perfluoropolymer materials (Table 3 and Table 4). For instance, Copolymer 3 achieves much greater hydrogen-methane selectivity than Cytop[®] and Hyflon[®] AD60, while its hydrogen permeance is greater than that of Cytop[®] and less than that of Hyflon[®] AD60. This suggests that Copolymer 3 is more size-sieving than the most selective of the commercial perfluoropolymers, Cytop[®], and can be used in a membrane with relatively high permeance. All of the polymers shown in Table 3 and Table 4 have carbon dioxide-hydrogen sulfide selectivities of more than 10. The polymers shown in Table 4 achieved wet mixed gas selectivities above 10.

TABLE 3 Pure gas permeance and selectivities for commercial perfluoropolymers and copolymers of Monomers D and H

Polymer	Permeance (gpu)				Selectivity for gases paired with CH ₄			
	N ₂	H ₂	He	CO ₂	N ₂	H ₂	He	CO ₂
Teflon [®] AF 2400	2,700	10,500	10,500	13,000	1.2	4.6	4.6	5.7
Hyflon [®] AD60	180	1,700	2,600	1,300	2.4	23	35	18
Cytop [®]	18	290	790	150	3.0	48	130	25
Copolymer 1	54	820	1,400	390	3.2	48	82	23
Copolymer 2	41	700	1,250	330	4.2	72	130	34
Copolymer 3	29	700	1,400	260	5.3	130	260	47

TABLE 4 Pure and mixed gas permeance and selectivities for membranes having commercial perfluoropolymers and copolymers of Monomers B and H

Membrane	Pure gas ^a			Mixed gas ^b		
	Permeance (gpu)	Selectivity		Permeance (gpu)	Selectivity	
	N ₂	CO ₂	CO ₂ /N ₂	H ₂ S	CO ₂	CO ₂ /H ₂ S
Hyflon [®] AD40	26	160	6.2	12.2	170	14
Hyflon [®] AD60	79	500	6.4	38	490	13
Copolymers of Monomers B and H	37	280	7.7	5.3	170	32

^a Pure feed gas at 50 psig feed pressure and 30 °C.

^b Mixed feed gas containing 33 mol % hydrogen sulfide in carbon dioxide at 50 psig and 30 °C (saturated with H₂O).

[00039] Membranes having the perfluoropolymers described in this specification can be designed to be used in membrane modules using conventional techniques. A few examples of suitable membrane module designs include spiral-wound modules, hollow fiber modules that use small polymeric capillaries or fibers that have the geometry of a shell and tube heat exchanger, and plate-and-frame modules. The membrane modules can also be configured to use a sweep gas on the permeate side of the membrane to improve separation. Multiple membrane modules can be manifolded together in a membrane separation unit to achieve a desired membrane area. According to at least one embodiment, the membrane modules and membrane stages can be in the absence of a hydrocarbon-selective membrane (e.g., a silicone rubber polydimethylsiloxane-type rubbery polymer or its equivalent); and the processes described in this disclosure can be carried out without using a hydrocarbon-selective membrane. According to at least one embodiment, the membrane modules and membrane stages can be in the absence of a hydrogen sulfide-selective membrane; and the processes described in this disclosure can be carried out without using a hydrogen sulfide-selective membrane.

[00040] In some embodiments, the membrane can have a carbon dioxide/hydrogen sulfide selectivity of at least 10 and a carbon dioxide permeance of at least 500 gpu. In some instances, membranes having carbon dioxide/hydrogen sulfide selectivity of 20 are used. In some instances, membranes having carbon dioxide/hydrogen sulfide selectivity of 30 are used. In some instances, the membrane can have carbon dioxide/hydrogen sulfide selectivity between about 10 and 30, preferably between about 20 and 30. According to at least one embodiment, the membrane can have carbon dioxide/hydrogen sulfide selectivity of at least 30.

[00041] A membrane stage can include one or multiple membrane modules in various configurations. Various membrane stage configurations are shown in Fig. 4: a single-pass membrane configuration in Fig. 4a; a two-stage configuration with retentate in series in Fig. 4b; a two-stage configuration with permeate in series in Fig. 4c; and a three-stage configuration in Fig. 4d. Each of the membrane stage configurations shown in Fig. 4 can be considered a membrane separation unit. These membrane separation units are capable of enriching hydrogen sulfide to at concentrations of 20–90 mol %. The minimum concentration of hydrogen sulfide that is suitable for processing in a Claus plant is about 20 mol %. A concentration of at least about 50 mol % is more desirable, and a concentration greater than about 90 mol % results in significant capital and operating cost savings.

[00042] Figure 4a is the simplest configuration with a single membrane stage. In Fig. 4a, feed-gas stream **401** is fed to single-pass membrane stage **410** where it is introduced to a carbon dioxide-selective membrane to obtain single-pass retentate stream **411** and single-pass permeate stream **412**; the single-pass retentate stream **411** and the single-pass permeate stream **412** being enriched in hydrogen sulfide and carbon dioxide respectively.

[00043] Figure 4b involves two membrane stages with retentate from the first stage being fed to the next stage. In Fig. 4b, feed-gas stream **401** can be combined with compressed second-stage permeate stream **433** to obtain mixed feed-gas stream **402**. Mixed feed-gas stream **402** is fed to first retentate-in-series membrane stage **420** where it is separated using a carbon dioxide-selective membrane to obtain first retentate-in-series retentate stream **421** and first retentate-in-series permeate stream **422**; the first retentate-in-series retentate stream **421** and the first retentate-in-series permeate stream **422** being enriched in hydrogen sulfide and carbon dioxide respectively. The first retentate-in-series retentate stream **421** is then introduced to second retentate-in-series membrane stage **430**, where it is separated using a carbon dioxide-selective membrane to obtain second retentate-in-series retentate stream **431** and second retentate-in-series permeate stream **432**; the second retentate-in-series retentate stream **431** and the second retentate-in-series permeate stream **432** being enriched in hydrogen sulfide and carbon dioxide respectively. The second retentate-in-series permeate stream **432** is compressed and combined with feed-gas stream **401** to be recycled through the process.

[00044] Figure 4c involves two membrane stages with permeate from the first stage being fed to the next stage. In Fig. 4c, feed-gas stream **401** is combined with second permeate-in-series retentate stream **451** from second permeate-in-series membrane stage **450** to obtain first-stage feed-gas stream **403**. The first-stage feed-gas stream **403** is introduced to first permeate-in-series membrane stage **440** where it is separated using a carbon dioxide-selective membrane to obtain first permeate-in-series retentate stream **441** and first permeate-in-series permeate stream **442**; the first permeate-in-series retentate stream **441** and the first permeate-in-series permeate stream **442** being enriched in hydrogen sulfide and carbon dioxide respectively. First permeate-in-series permeate stream **442** is compressed and then introduced to second permeate-in-series membrane stage **450** where it is separated using a carbon dioxide-selective membrane to obtain second permeate-in-series retentate stream **451** and second permeate-in-series permeate stream **452**; the second permeate-in-series retentate stream **451** and the second permeate-in-series permeate stream **452** being enriched in hydrogen sulfide and

carbon dioxide respectively. The second permeate-in-series retentate stream **451** is then combined with feed-gas stream **401**.

[00045] Figure 4d is an illustration of a system and process that combines elements of the systems and processes shown in Fig. 4b and 4c. It includes three membrane stages and three steps, with retentate and permeate from the first stage being processed separately in the other two stages. In Fig. 4d, feed-gas stream **401** is combined with second membrane-stage permeate stream **472** and third membrane-stage retentate stream **481** from second membrane stage **470** and third membrane stage **480** respectively to obtain mixed feed-gas stream **404**. Mixed feed-gas stream **404** is introduced to first membrane stage **460** where it is separated in the presence of a carbon dioxide-selective membrane to obtain first retentate stream **461** and first permeate stream **462**.

[00046] First retentate stream **461** is then introduced to second membrane stage **470** where it is separated using a carbon dioxide-selective membrane to obtain second membrane-stage retentate stream **471** and second membrane-stage permeate stream **472**. Second membrane-stage retentate stream **471** is enriched in hydrogen sulfide and can be sent to a sulfur recovery unit. Second membrane-stage permeate stream **472** is enriched in carbon dioxide; it is compressed and combined with feed-gas stream **401** to be recycled through the system.

[00047] First permeate stream **462** is compressed and then fed to third membrane stage **480** where it is separated using a carbon dioxide-selective membrane to obtain third membrane-stage retentate stream **481** and third membrane-stage permeate stream **482**. The third membrane-stage permeate stream **482** is enriched in carbon dioxide and can be treated to remove any remaining hydrogen sulfide, or in some instances captured for use in appropriate industrial applications or discharged into the atmosphere. The third membrane-stage retentate stream **481** can be combined with the feed-gas stream **401** to be recycled through the system.

[00048] Each of the processes illustrated in Fig. 4 produce streams that are stripped of hydrogen sulfide. Typically, these hydrogen sulfide-stripped streams can contain between about 0.1 and 0.15 mol % (1,000–1,500 ppm) hydrogen sulfide, alternately between about 0.01 and 0.015 mol % (100–150 ppm) hydrogen sulfide. In some locations, such streams can be safely discharged to the atmosphere after catalytic or thermal oxidation to convert remaining hydrogen sulfide to sulfur dioxide. According to at least one embodiment, the hydrogen sulfide-stripped stream can be sent directly to a catalytic converter of the sulfur recovery unit.

According to at least one embodiment, the hydrogen sulfide-stripped stream can be used in enhanced oil recovery operations. Streams with a concentration of hydrogen sulfide greater than about 0.1–0.15 mol % can be treated to remove at least some remaining hydrogen sulfide using a polishing step. Such processes can include chemical polishing (such as a reaction of hydrogen sulfide with zinc oxide), molecular sieve adsorption, or a selective amine absorption process. The polished gas can be catalytically or thermally oxidized and discharged, and the stripped hydrogen sulfide can be recycled. In some instances, the stream that is stripped of hydrogen sulfide needs no further polishing after the membrane separation step.

[00049] The processes illustrated in Fig. 4 were simulated to illustrate some of their features. The processes were simulated using a feed gas containing 2 mol % hydrogen sulfide and using enough membrane to produce a residue gas containing 20 mol % hydrogen sulfide, 50 mol % hydrogen sulfide, and 90 mol % hydrogen sulfide. The membranes used were assumed to have 500 gpu carbon dioxide permeance and 16.7, 25, 50, or 100 gpu hydrogen sulfide permeance. This results in carbon dioxide-hydrogen sulfide selectivity of 30, 20, 10, or 5. Each of the processes was capable of producing a stream with a concentration of hydrogen sulfide between about 20 and 90 mol %. The lower limit is the minimum concentration of hydrogen sulfide suitable for a feed to a Claus plant. Claus plant efficiency generally increases with greater concentration of hydrogen sulfide. In some instances a concentration greater than about 90 mol % hydrogen sulfide can be achieved. According to at least one embodiment, the concentration of hydrogen sulfide in a hydrogen sulfide-enriched stream from a membrane separation unit can be between about 90 and 99.5 mol %, alternately between about 95 and 99.5 mol %, alternately between about 97 and 99.5 mol %. Significant capital and operating cost savings can be achieved using a feed gas to a Claus plant that contains greater than 90 mol % hydrogen sulfide.

[00050] To illustrate the process of Fig. 4a, a feed-gas containing 2 mol % hydrogen sulfide and 98 mol % carbon dioxide was fed to a process having the configuration shown in Fig. 4a at a rate of 1,000 m³/h and 15 bar pressure. The single-pass permeate stream **412** was fixed at 1 bar pressure. The results show that the residual concentration of hydrogen sulfide in single-pass retentate stream **411** decreases as membrane selectivity increases from 5–30. But even at 30 selectivity and with only 20 mol % hydrogen sulfide in the feed-gas stream **401**, the single-pass retentate stream **411** still has a concentration of hydrogen sulfide (0.2 mol %) that is not suitable for venting to the atmosphere after catalytic or thermal oxidation. In these instances,

the single-pass retentate stream **411** must be treated to reduce the concentration of hydrogen sulfide to an acceptable level, or it must be recycled to a convenient stage in the gas treatment plant.

[00051] The single-pass membrane configuration shown in Fig. 4a is the simplest, least costly configuration, but may not be suitable for producing a hydrogen sulfide-stripped stream that can be safely discharged or used in other applications without undergoing any additional hydrogen sulfide separation unless more selective membranes are used. For a feed gas having 2 mol % hydrogen sulfide, a suitable configuration would be capable of producing a permeate stream with a molar concentration of hydrogen sulfide reduced by at least a factor of 5, preferably at least a factor of 10. With membrane selectivity of 5 and 10, the molar concentration of hydrogen sulfide is only reduced by a factor of about 1.2–4 (Table 5).

TABLE 5 Single-pass membrane configuration performance:
H₂S recovery using a feed-gas stream containing 2 mol % H₂S

Selectivity	H ₂ S in single-pass permeate stream 412 (mol %)	Recovered H ₂ S (%) ^a	Membrane area (m ²)
<i>Twenty mole percent H₂S in single-pass retentate stream</i>			
5	1.03	51	52
10	0.56	74	51
20	0.29	87	51
30	0.2	91	51
<i>Fifty mole percent H₂S in single-pass retentate stream</i>			
5	1.32	35	55
10	0.77	62	55
20	0.41	80	55
30	0.28	86	55
<i>Ninety mole percent H₂S in single-pass retentate stream</i>			
5	1.64	18	56
10	1.09	46	58
20	0.63	69	58
30	0.45	78	58

^a Percent H₂S from the feed-gas stream that is recovered in the single-pass retentate stream.

[00052] To illustrate the process of Fig. 4b, a feed-gas containing 2 mol % hydrogen sulfide and 98 mol % carbon dioxide was fed to a process having the configuration shown in Fig. 4b (Table 6). In this configuration, the first retentate-in-series permeate stream 422 contains about 0.1–0.3 mol % hydrogen sulfide. The first retentate-in-series retentate stream 421 has about 5 mol % hydrogen sulfide and is processed in second retentate-in-series membrane stage 430 to obtain 20–90 mol % hydrogen sulfide in second retentate-in-series retentate stream 431, which includes 85–95% of hydrogen sulfide from feed-gas stream 401 (Table 6). The second retentate-in-series permeate stream 432 contains about 2 mol % hydrogen sulfide, which is similar to the concentration of hydrogen sulfide in the feed-gas stream 401; an efficient use of this stream is to combine it with feed-gas stream 401 to be recycled through the process. This configuration is suitable for producing a hydrogen sulfide-stripped stream that can be safely discharged or used in other applications without additional hydrogen sulfide separation when membranes having carbon dioxide-hydrogen sulfide selectivity of 20 or more are used; membranes with less selectivity may be unsuitable for this purpose.

TABLE 6 Two-stage retentate-in-series configuration performance: H₂S recovery using a feed-gas stream containing 2 mol % H₂S

Selectivity	H ₂ S in first retentate-in- series permeate stream 422	Recovered H ₂ S (%) ^a	Membrane area (m ²)		Theoretical compressor power (kW)
	(mol %)		MS	MS	
			420	430	
<i>Twenty mole percent H₂S in second retentate-in-series retentate stream</i>					
5	0.65	70	51	20	38
10	0.31	86	50	19	35
20	0.15	93	49	18	34
30	0.10	96	49	18	33
<i>Fifty mole percent H₂S in second retentate-in-series retentate stream</i>					
5	0.71	65	53	33	59
10	0.32	85	53	27	48
20	0.15	93	52	25	43
30	0.10	95	52	24	41
<i>Ninety mole percent H₂S in second retentate-in-series retentate stream</i>					
5	0.82	59	54	61	109
10	0.35	83	54	40	68
20	0.16	92	54	33	53
30	0.10	95	53	31	49

MS, membrane stage

^a Percent H₂S from the feed-gas stream that is recovered in the second retentate-in-series retentate stream.

[00053] To illustrate the process of Fig. 4c, a feed-gas containing 2 mol % hydrogen sulfide and 98 mol % carbon dioxide was fed to a process having the configuration shown in Fig. 4c.

In this configuration, the process was simulated to achieve 20, 50, and 90 mol % hydrogen sulfide concentration in first permeate-in-series retentate stream 441 (Table 7). After processing in first permeate-in-series membrane stage 440, the stream 442 was compressed to increase pressure from 1 bar to 15 bar and then sent to second permeate-in-series membrane stage 450. The second permeate-in-series retentate stream 451, which contained about 2 mol % hydrogen sulfide, was combined with the feed-gas stream 401 to be recycled through the process. About 95–99% of the hydrogen sulfide in feed-gas stream 401 was concentrated in first permeate-in-series retentate stream 441, and only a few percent ends up in second permeate-in-series permeate stream 452 (Table 7).

[00054] Using membranes in this configuration with carbon dioxide-hydrogen sulfide selectivity of at least 10 produces a second permeate-in-series permeate stream 452 that has a sufficiently low concentration of hydrogen sulfide to allow safe discharge without further treatment (other than catalytic or thermal oxidation). For example, the second permeate-in-series permeate stream 452 has only 200–600 ppm hydrogen sulfide if membranes with carbon dioxide-hydrogen sulfide selectivity of at least 20 are used in this configuration. But the improvement comes at the cost of a significant increase in membrane area and compressor power as compared with simpler configurations.

TABLE 7 Two-stage permeate-in-series configuration performance: H₂S recovery using a feed-gas stream containing 2 mol % H₂S

Selectivity	H ₂ S in second permeate-in-series permeate stream 452 (mol %)	Recovered H ₂ S (%) ^a	Membrane area (m ²)		Theoretical compressor power (kW)
			MS 440	MS 450	
<i>Twenty mole percent H₂S in first permeate-in-series retentate stream</i>					
5	0.30	86	89	49	177
10	0.10	95	66	48	146
20	0.035	98	58	48	128
30	0.018	99	55	48	122
<i>Fifty mole percent H₂S in first permeate-in-series retentate stream</i>					
5	0.34	83	131	52	259
10	0.13	94	83	52	179
20	0.044	98	68	51	145
30	0.022	99	63	51	136
<i>Ninety mole percent H₂S in first permeate-in-series retentate stream</i>					
5	0.39	81	251	53	527
10	0.16	92	99	53	242
20	0.057	97	83	52	170
30	0.031	98	74	52	152

^a Percent H₂S from the feed-gas stream that is recovered in the second retentate-in-series retentate stream.

[00055] To illustrate the process of Fig. 4d, a feed-gas containing 2 mol % hydrogen sulfide and 98 mol % carbon dioxide was fed to a process having the configuration shown in Fig. 4d.

The process in this configuration was simulated to achieve 20, 50, and 90 mol % hydrogen sulfide concentration in second membrane-stage retentate stream **471** (Table 8). In the simulations, the first retentate stream **461** had 10 mol % hydrogen sulfide. The two recycle streams, second membrane-stage permeate stream **472** and third membrane-stage retentate stream **481**, each had 2 mol % hydrogen sulfide. The first retentate stream **461** contained 10 mol % hydrogen sulfide. When membranes having carbon dioxide-hydrogen sulfide selectivity of at least 10 are used, the process achieves suitable hydrogen sulfide concentration in the third membrane-stage permeate stream **482** to safely discharge the stream with no further treatment (other than catalytic or thermal oxidation). This configuration was capable of concentrating hydrogen sulfide in the second membrane-stage retentate stream **471** to about 90 mol % while recovering about 95–99% of the hydrogen sulfide from the feed-gas stream **401** (Table 8). In this process, the molar concentration of hydrogen sulfide in the feed-gas stream **401** is reduced by a factor of 20–30 compared with the concentration of hydrogen sulfide in the third membrane-stage permeate stream **482**.

TABLE 8 Three-stage configuration performance: H₂S recovery using a feed-gas stream containing 2 mol % H₂S

Selectivity	H ₂ S in third	Recovered	Membrane area (m ²)			Theoretical	
	MS permeate		MS	MS	MS	compressor	
	stream 482	H ₂ S				Unit	Unit
	(mol %)	(%) ^a	460	470	480	465	475
<i>Twenty mole percent H₂S in second MS retentate stream</i>							
5	0.27	88	76	49	8	166	15
10	0.089	96	61	82	7	135	14
20	0.028	99	55	48	7	123	13
30	0.014	99	53	93	7	119	13
<i>Fifty mole percent H₂S in second MS retentate stream</i>							
5	0.29	86	88	52	18	191	31
10	0.091	96	65	81	14	145	24
20	0.028	99	59	51	12	130	21
30	0.014	99	57	94	12	126	21
<i>Ninety mole percent H₂S in second MS retentate stream</i>							
5	0.32	84	108	53	39	235	64
10	0.099	95	69	78	24	152	36
20	0.030	99	60	90	19	133	28
30	0.015	99	58	93	18	128	25

MS, membrane stage

^a Percent H₂S from the feed-gas stream that is recovered in the second retentate-in-series retentate stream.

[00056] The processes summarized in Tables 5–8 were carried out using a feed gas containing 2 mol % hydrogen sulfide. To illustrate the effectiveness of the processes with a

feed having a greater concentration of hydrogen sulfide, additional simulations were carried out using a feed gas having about 10 mol % hydrogen sulfide.

[00057] The process of Fig. 4a was carried out using a feed gas with 10 mol % hydrogen sulfide and 90 mol % carbon dioxide (Table 9). In this configuration, even the most selective membrane for carbon dioxide-hydrogen sulfide separation (20) used with the lowest concentration of hydrogen sulfide (20 mol %) was not able to sufficiently reduce the concentration of hydrogen sulfide in the single-pass permeate stream 412 to allow safe discharge into the atmosphere without further treatment (other than by catalytic or thermal oxidation) (Table 9). However, this configuration can still be used with an additional polishing step.

TABLE 9 Single-pass membrane configuration performance:
H₂S recovery using a feed-gas stream containing 10 mol % H₂S

Selectivity	H ₂ S in single-pass permeate stream 412 (mol %)	Recovered H ₂ S (%) ^a	Membrane area (m ²)
<i>Twenty mole percent H₂S in single-pass retentate stream</i>			
5	3.3	80	36
10	1.7	91	33
20	0.9	95	32
30	0.6	97	32
<i>Fifty mole percent H₂S in single-pass retentate stream</i>			
5	5.1	55	57
10	2.8	76	56
20	1.4	88	56
30	1.0	92	55
<i>Ninety mole percent H₂S in single-pass retentate stream</i>			
5	7.4	29	66
10	4.7	56	70
20	2.7	76	73
30	1.9	83	74

^a Percent H₂S from the feed-gas stream that is recovered in the single-pass retentate stream.

[00058] The process of Fig. 4b was carried out using a feed gas having 10 mol % hydrogen sulfide and 90 mol % carbon dioxide (Table 10). The first retentate-in-series membrane stage **420** produces a retentate stream, first retentate-in-series retentate stream **421**, which has 20 mol % hydrogen sulfide. Between about 92–98% of the hydrogen sulfide from the feed gas is recovered and concentrated in second retentate-in-series retentate stream **431** after

processing in the second retentate-in-series membrane stage **430** (Table 10). This stream is sent to a sulfur recovery unit to be processed for sulfur recovery. Between about 0.2–0.9 mol % hydrogen sulfide remains in the second retentate-in-series permeate stream **432** making it unsuitable for discharging into the atmosphere without further treatment.

TABLE 10 Two-stage retentate-in-series configuration performance: H₂S recovery using a feed-gas stream containing 10 mol % H₂S

Selectivity	H ₂ S in first retentate-in- series permeate stream 422 (mol %)	Recovered H ₂ S (%) ^a	Membrane area (m ²)		Theoretical compressor power (kW)
			MS 420	MS 430	
<i>Fifty mole percent H₂S in second retentate-in-series retentate stream</i>					
5	3.21	73	51	28	45
10	0.91	93	47	68	119
20	0.44	96	46	61	105
30	0.29	98	46	59	101
<i>Ninety mole percent H₂S in second retentate-in-series retentate stream</i>					
5	3.67	66	56	70	100
10	0.94	92	52	114	175
20	0.44	96	51	93	134
30	0.29	97	51	87	123

MS, membrane stage

^a Percent H₂S from the feed-gas stream that is recovered in the second retentate-in-series retentate stream.

[0060] The process of Fig. 4c was simulated using a feed gas having 10 mol % hydrogen sulfide and 90 mol % carbon dioxide (Table 11). The second permeate-in-series membrane stage 450 produced a second permeate-in-series retentate stream 451 having 10 mol % hydrogen sulfide. In this configuration, the process is capable of producing a hydrogen sulfide-

enriched stream, first permeate-in-series retentate stream 441, with a concentration of hydrogen sulfide that is sufficiently high to be processed in the Claus plant of a sulfur recovery unit. The process is also capable of producing a hydrogen sulfide-stripped stream, second permeate-in-series permeate stream **452**, that has a sufficiently low concentration of hydrogen sulfide to be safely discharged to the atmosphere without further treatment (other than by catalytic or thermal oxidation).

TABLE 11 Two-stage permeate-in-series configuration performance: H₂S recovery using a feed-gas stream containing 10 mol % H₂S

Selectivity	H ₂ S in second permeate-in- series permeate stream 452	Recovered H ₂ S (%) ^a	Membrane area (m ²)		Theoretical compressor power (kW)
	(mol %)		MS	MS	
			440	450	
<i>Twenty mole percent H₂S in first permeate-in-series retentate stream</i>					
5	1.18	94	42	29	85
10	0.39	98	36	28	74
20	0.13	99	34	27	68
30	0.063	99.7	33	27	67
<i>Fifty mole percent H₂S in first permeate-in-series retentate stream</i>					
5	1.55	87	90	46	168
10	0.54	96	70	45	131
20	0.18	99	62	44	114
30	0.093	99.2	60	44	109
<i>Ninety mole percent H₂S in first permeate-in-series retentate stream</i>					
5	1.94	82	191	52	331
10	0.75	93	117	51	190
20	0.27	97	94	50	145
30	0.143	98.7	88	49	133

^a Percent H₂S from the feed-gas stream that is recovered in the second retentate-in-series retentate stream.

[00061] The process of Fig. 4d was also simulated using a feed gas having 10 mol % hydrogen sulfide and 90 mol % carbon dioxide (Table 12). In this simulation, the first retentate stream **461** contained 20 mol % hydrogen sulfide. The two recycle streams, second membrane-

stage permeate stream **472** and third membrane-stage retentate stream **481**, each contained 10 mol % hydrogen sulfide. The process was capable of producing a hydrogen sulfide-enriched stream, second membrane-stage retentate stream **471**, suitable for sending to the Claus plant of a sulfur recovery unit. The process was also capable of producing a hydrogen sulfide-stripped stream, third membrane-stage permeate stream **482** suitable for safely discharging to the atmosphere without additional treatment (other than catalytic or thermal oxidation). In some instances, the process was also capable of recovering as much as 99–99.5% of hydrogen sulfide from the feed gas and concentrating it in second membrane-stage retentate stream **471**. However, this configuration required the most membrane area and compressor power of the configurations shown in Fig. 4.

TABLE 12 Three-stage configuration performance: H₂S recovery using a feed-gas stream containing 10 mol % H₂S

Selectivity	H ₂ S in third MS permeate stream 482 (mol %)	Recovered H ₂ S (%) ^a	Membrane area (m ²)			Theoretical compressor power (kW)	
			MS	MS	MS	Unit	Unit
			460	470	480	465	475
<i>Fifty mole percent H₂S in second MS retentate stream</i>							
5	1.16	90	64	34	45	129	56
10	0.367	97	55	29	44	112	45
20	0.114	99	52	26	43	105	40
30	0.057	99.5	51	25	43	103	39
<i>Ninety mole percent H₂S in second MS retentate stream</i>							
5	1.26	88	75	95	50	151	134
10	0.384	97	62	64	49	125	78
20	0.115	99	58	53	48	116	60
30	0.057	99.5	56	51	48	114	55

MS, membrane stage

^a Percent H₂S from the feed-gas stream that is recovered in the second retentate-in-series retentate stream.

[00062] Sulfur recovery can be carried out using a variety of techniques and processes. An example of a common process for recovering sulfur is the Claus process. Another example of a sulfur recovery process is generally referred to as liquid phase oxidation, which involves converting hydrogen sulfide to sulfur in the liquid phase in the presence of an oxidant. Liquid phase oxidation is typically carried out in the presence of a catalyst.

[00063] An embodiment of a process for enriching hydrogen sulfide in a sour gas for feed to a sulfur recovery unit can include the steps of: providing a sour gas having carbon dioxide and hydrogen sulfide, separating the sour gas in a membrane separation unit to obtain hydrogen

sulfide-enriched gas and hydrogen sulfide-stripped gas, and processing the hydrogen sulfide-enriched gas in a sulfur recovery unit. By reducing the overall flow of gas to the sulfur recovery unit, relatively smaller equipment can be used in the sulfur recovery process and in subsequent tail gas treatment processes.

[00064] The process of enriching hydrogen sulfide for feed to a sulfur recovery unit can also include using nonselective amine absorption, selective amine absorption, or both to further enrich the hydrogen sulfide-enriched stream or to reduce the concentration of hydrogen sulfide in the hydrogen sulfide-stripped stream. According to at least one embodiment, the process can include separating the sour gas using nonselective amine absorption to obtain an overhead gas and a recovered sour gas and sending the recovered sour gas to the membrane separation unit. According to at least one embodiment, the process can include separating the sour gas using selective amine absorption, and sending the recovered sour gas to the membrane separation unit. According to at least one embodiment, the process can include processing the sour gas in the membrane separation unit and sending the hydrogen sulfide-stripped stream to a selective amine absorption unit to obtain overhead gas and recovered hydrogen sulfide. The recovered hydrogen sulfide can be recycled to the membrane separation unit, and the overhead gas can be polished to remove remaining hydrogen sulfide, oxidized and vented to the atmosphere, or simply vented to the atmosphere.

[00065] The step of processing the hydrogen sulfide-rich gas in a sulfur recovery unit includes introducing the hydrogen sulfide-rich gas to a process unit for the purpose of recovering sulfur from sulfur compounds in the hydrogen sulfide-rich gas. In certain embodiments, the sulfur recovery unit can include a Claus unit. The high concentration of hydrogen sulfide in the hydrogen sulfide-rich gas allows the sulfur recovery unit to operate more efficiently. In some embodiments, heat energy from the oxidation of hydrogen sulfide in the hydrogen sulfide-rich gas is sufficient to destroy other minor components in the hydrogen sulfide-rich gas, such as mercaptans, benzene, toluene, and xylene. The destruction of benzene, toluene, and xylene in the sulfur recovery unit can improve sulfur recovery in the sulfur recovery unit and reduce foaming and other associated problems in subsequent tail gas treatment processes (e.g., amine absorption). And because high concentrations of hydrogen sulfide can be achieved in hydrogen sulfide-rich gas by membrane separation alone, conventional amine absorption processes for enriching hydrogen sulfide fed to a sulfur

recovery unit can be avoided; significantly simplifying operations and reducing capital expenses.

[00066] The description can use the phrases “in some embodiments,” “in various embodiments,” “in an embodiment,” or “in embodiments,” which can each refer to one or more of the same or different embodiments. Furthermore, the terms “comprising,” “including,” “having,” and the like, as used with respect to embodiments of the present disclosure, are synonymous.

[00067] Unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims should be understood as being modified by the term “about.” The term “about” applies to all numeric values, whether or not explicitly indicated. “About” generally refers to a range of numbers that a person of ordinary skill in the art would consider a reasonable amount of deviation to the recited values.

[00068] Ranges can be expressed in this disclosure as from about one particular value and to about another particular value. With these ranges, another embodiment is from the one particular value and/or to the other particular value, along with all combinations within the range. When the range of values is described or referenced in this disclosure, the interval encompasses each intervening value between the upper limit and the lower limit as well as the upper limit and the lower limit and includes smaller ranges of the interval subject to any specific exclusion provided.

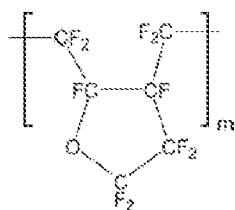
CLAIMS

We claim:

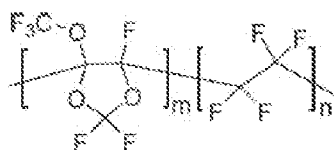
1. A process for recovering sulfur from a sour gas, the process comprising the steps of:
providing the sour gas to a membrane separation unit having a membrane stage that comprises a carbon dioxide-selective membrane, the carbon dioxide-selective membrane comprising a perfluoropolymer, and wherein the sour gas comprises carbon dioxide and at least 1 mol % hydrogen sulfide;
separating the sour gas using the carbon dioxide-selective membrane in the membrane separation stage to obtain hydrogen sulfide-enriched gas and hydrogen sulfide-stripped gas, wherein the hydrogen sulfide-enriched gas has a hydrogen sulfide concentration of at least 20 mol %, and wherein the hydrogen sulfide-stripped gas comprises carbon dioxide; and
processing the hydrogen sulfide-enriched gas in a sulfur recovery unit to obtain sulfur.
2. The process of claim 1, wherein the hydrogen sulfide-stripped gas further comprises residual hydrogen sulfide, and wherein the process further comprises the steps of:
oxidizing the hydrogen sulfide-stripped gas in an oxidizer such that residual hydrogen sulfide in the hydrogen sulfide-stripped gas is reacted with oxygen to produce sulfur dioxide-bearing gas.
3. The process of claim 1 or 2, further comprising the step of:
venting the sulfur dioxide-bearing gas to the atmosphere.
4. The process of any preceding claim, further comprising the step of:
capturing the sulfur dioxide-bearing gas for use in enhanced oil recovery operations.
5. The process of any preceding claim, wherein the hydrogen sulfide-stripped gas has a concentration of hydrogen sulfide that is less than 0.1 mol %.
6. The process of any preceding claim, wherein the hydrogen sulfide-stripped gas has a concentration of hydrogen sulfide that is less than 0.015 mol %.
7. The process of any preceding claim, wherein the hydrogen sulfide-stripped gas has a

concentration of hydrogen sulfide that is less than 0.01 mol %.

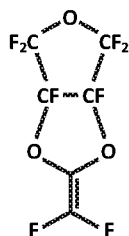
8. The process of any preceding claim, wherein the hydrogen sulfide-enriched gas has a concentration of hydrogen sulfide that is greater than 80 mol %.
9. The process of any preceding claim, wherein the hydrogen sulfide-enriched gas has a concentration of hydrogen sulfide that is greater than 90 mol %.
10. The process of any preceding claim, wherein the hydrogen sulfide-enriched gas has a concentration of hydrogen sulfide that is greater than 95 mol %.
11. The process of any preceding claim, wherein the carbon dioxide-selective membrane has carbon dioxide-hydrogen sulfide selectivity greater than 10.
12. The process of any preceding claim, wherein the carbon dioxide-selective membrane has carbon dioxide-hydrogen sulfide selectivity greater than 20.
13. The process of any preceding claim, wherein the carbon dioxide-selective membrane has carbon dioxide-hydrogen sulfide selectivity greater than 30.
14. The process of any preceding claim, wherein the membrane separation unit comprises a single-pass membrane stage configuration.
15. The process of any of claims 1–13, wherein the membrane separation unit comprises a two-stage retentate-in-series membrane configuration.
16. The process of any of claims 1–13, wherein the membrane separation comprises a two-stage permeate-in-series membrane configuration.
17. The process of any of claims 1–13, wherein the membrane separation unit comprises a three-stage membrane configuration.
18. The process of any preceding claim, wherein the perfluoropolymer comprises a monomer having the chemical structure:



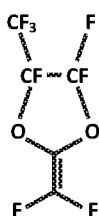
19. The process of any of claims 1–17, wherein the perfluoropolymer comprises a monomer having the chemical structure:



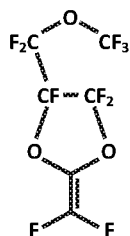
20. The process of any of claims 1–17, wherein the perfluoropolymer comprises a monomer having a chemical structure selected from the group consisting of



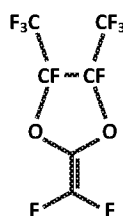
A



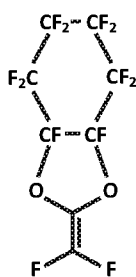
B



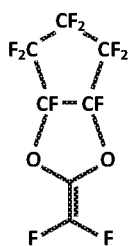
C



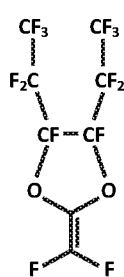
D



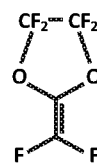
E



F



G



H

and combinations of the same.

1/4

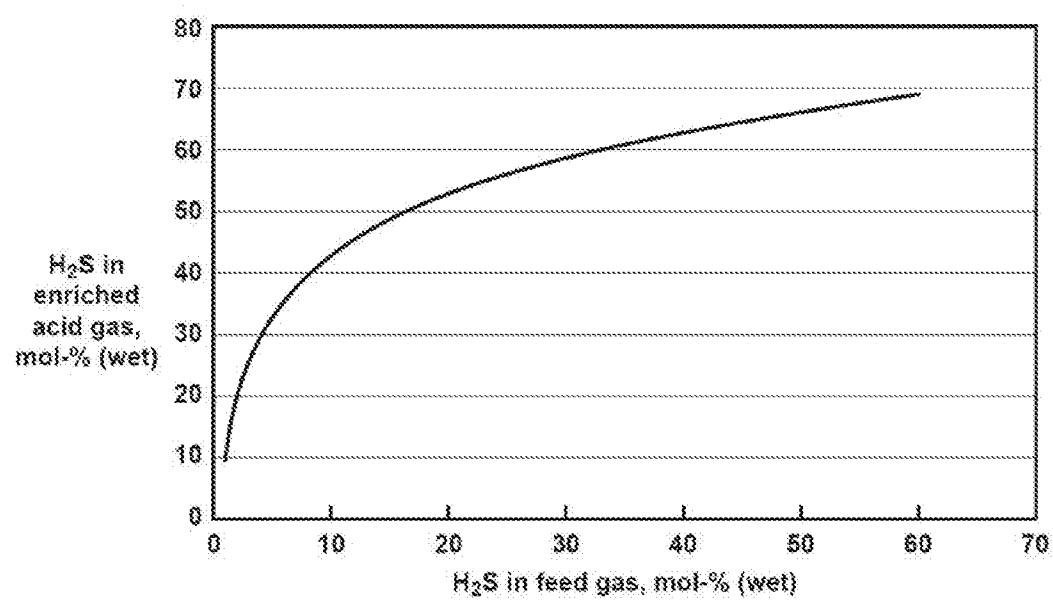


FIG. 1

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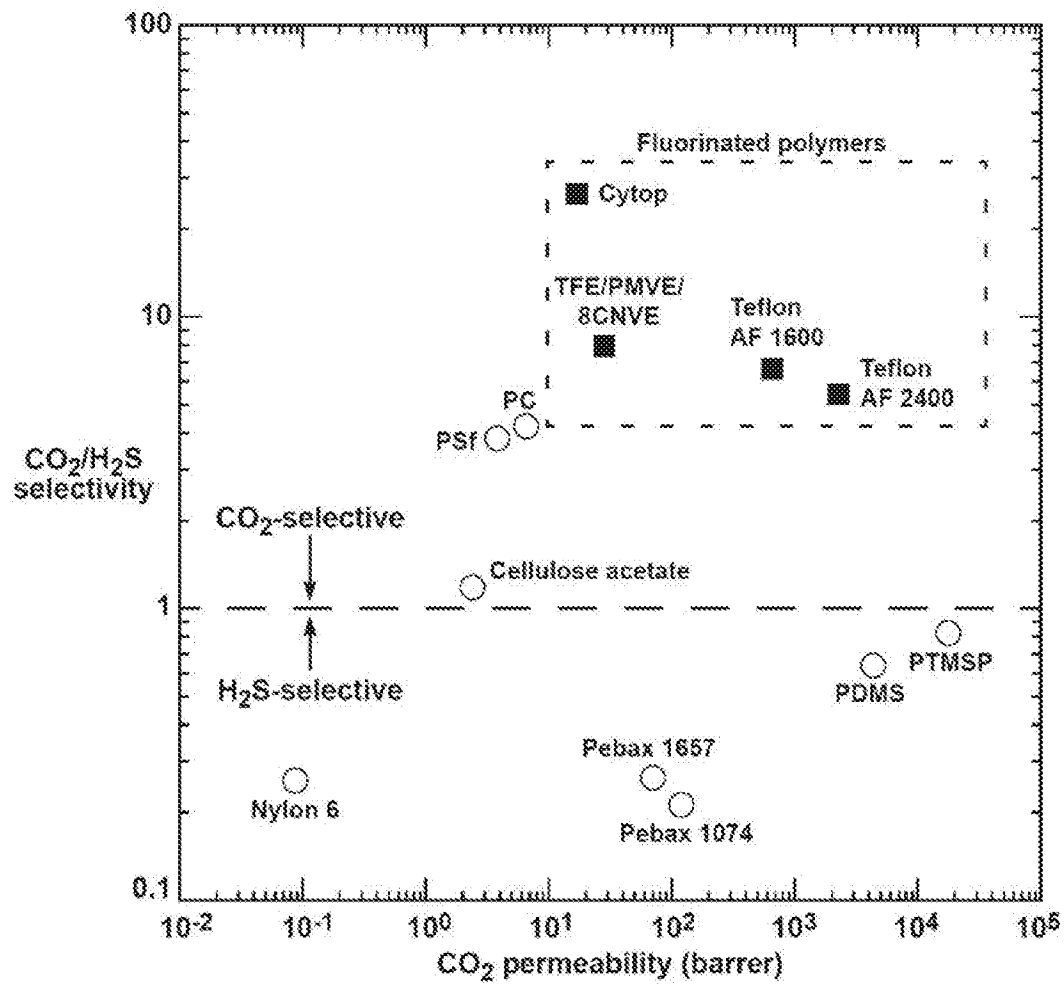
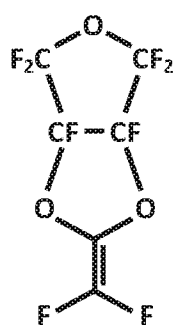
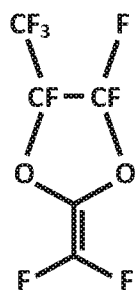


FIG. 2

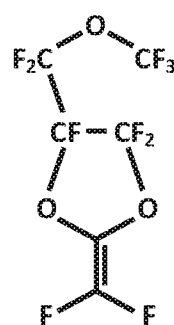
3/4



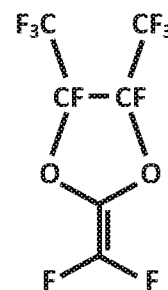
A



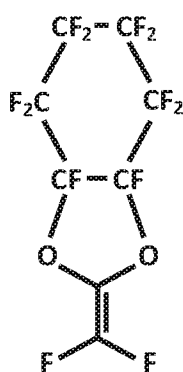
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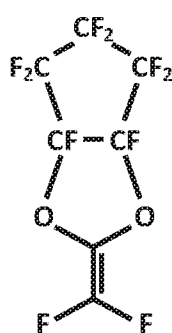
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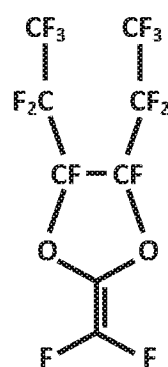
D



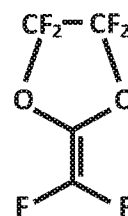
E



F



G

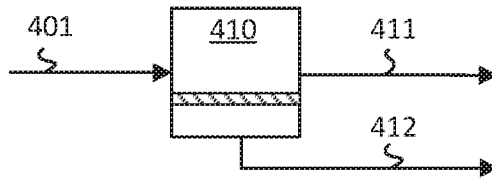


H

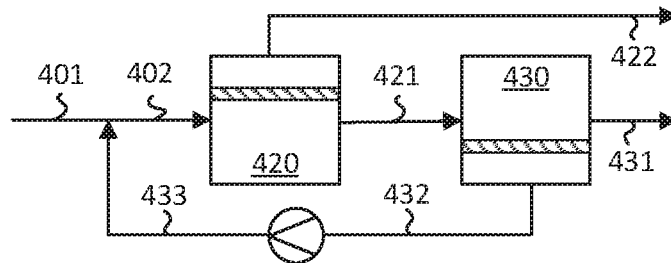
FIG. 3

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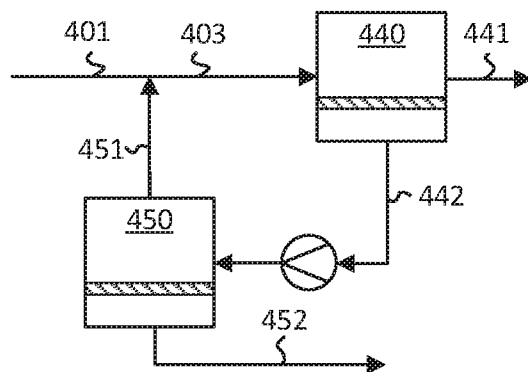
4a)



4b)



4c)



4d)

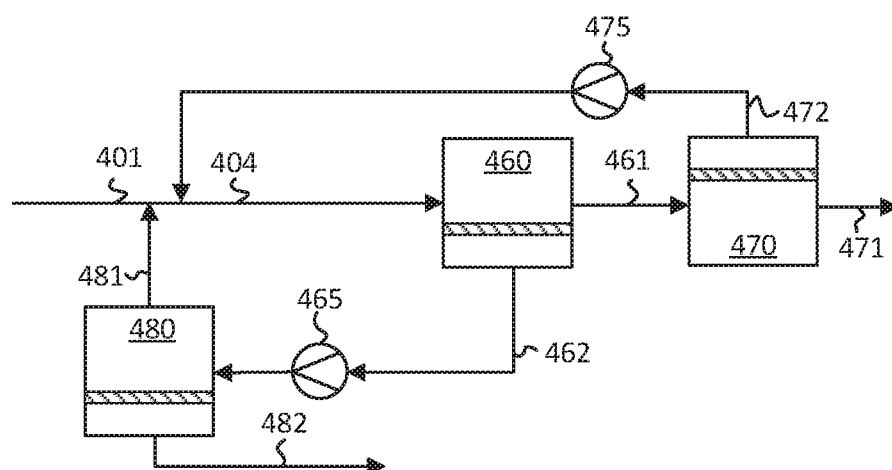


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/033326

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	D WANG ET AL: "Selective removal of trace H ₂ S from gas streams containing CO ₂ using hollow fibre membrane modules/contractors", SEPARATION AND PURIFICATION TECHNOLOGY, vol. 35, no. 2, 15 February 2004 (2004-02-15), pages 125-131, XP055721778, NL ISSN: 1383-5866, DOI: 10.1016/S1383-5866(03)00135-7	1,5-14
Y	see, in particular figures 1,2,3,4,5,6,7,8,9; page 126, left col. lines 25-27; and points: 2.1 "Hollow fibre module"; 2.2 "Experimental procedure and 4. "Conclusions" ----- -/--	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

11 September 2020

Date of mailing of the international search report

21/09/2020

Name and mailing address of the ISA/

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NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

Rumbo, Angel

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/033326

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHOULIANG YI ET AL: "Ultrasselective glassy polymer membranes with unprecedented performance for energy-efficient sour gas separation", SCIENCE ADVANCES, vol. 5, no. 5, 1 May 2019 (2019-05-01), page eaaw5459, XP055721784, DOI: 10.1126/sciadv.aaw5459	1,5-14
Y	see, in particular figures 1 E,F; 2 A,B,E,F and 3; see also page 2 of 11 , right column ,lines 28-34 and 40-42	1-20
Y	Kartik Ramasubramanian: "CO 2 (H 2 S)-SELECTIVE MEMBRANES FOR FUEL CELL HYDROGEN PURIFICATION AND FLUE GAS CARBON CAPTURE: AN EXPERIMENTAL AND PROCESS MODELING STUDY", 31 December 2013 (2013-12-31), XP055723138, Retrieved from the Internet: URL:https://etd.ohiolink.edu/!etd.send_file?accession=osu1480453792157218&disposition=inlinehttps://etd.ohiolink.edu/!etd.send_file?accession=osu1374193903&disposition=attachment [retrieved on 2020-08-17] see in particular figure 1.2; see tables 2.1 to 2.5; see also tables 4.1-4.4 and figures 4.1 to 4.8	1-20
Y	Varun Vakharia: "Development of Membrane Technology for CO 2 Removal and H 2 Purification: A Techno-Economic, Lab-Scale, and Pilot-Scale Study", https://etd.ohiolink.edu/!etd.send_file?accession=osu1480453792157218&disposition=inline, 31 December 2016 (2016-12-31), pages 1-198, XP055723139, The Ohio State University Retrieved from the Internet: URL:https://etd.ohiolink.edu/!etd.send_file?accession=osu1480453792157218&disposition=inline [retrieved on 2020-08-17] see, in particular, figure 2.6 at page 42;see also figure 2.2-2.5 and tables 2.1 to 2.6	1-20
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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2020/033326

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Jay Kniep ET AL: "FIELD TESTS OF MTR MEMBRANES FOR SYNGAS SEPARATIONS: Final Report of CO₂-Selective Membrane Field Test Activities at the National Carbon Capture Center", 15 December 2017 (2017-12-15), XP055723142, Retrieved from the Internet: URL:https://static1.squarespace.com/static/566b0ac3df40f3a731712cf4/t/5c631e56419202ec4a7d5d7b/1549999704016/MTR+CO2+Membranes+-+Final+Report.pdf [retrieved on 2020-08-17] see, in particular, figures 7 and 10-15 -----	1-20
Y	ARCELLA V ET AL: "A study on a perfluoropolymer purification and its application to membrane formation", JOURNAL OF MEMBRANE SCIENCE, ELSEVIER BV, NL, vol. 163, no. 2, 1 November 1999 (1999-11-01), pages 203-209, XP004182027, ISSN: 0376-7388, DOI: 10.1016/S0376-7388(99)00184-2 see table 1 Hyflon AD 60X CO₂ permeability. -----	1-20
Y	DAVID F. SANDERS ET AL: "Energy-efficient polymeric gas separation membranes for a sustainable future: A review", POLYMER, vol. 54, no. 18, 4 July 2013 (2013-07-04), pages 4729-4761, XP055724415, GB ISSN: 0032-3861, DOI: 10.1016/j.polymer.2013.05.075 see, in particular, point 6.3 "perfluoropolymers" and figure 31 -----	1-20
A	SEYED MOJTABA MIRFENDERESKI ET AL: "Selective Removal of H₂S from Gas Streams with High CO₂ Concentration Using Hollow-Fiber Membrane Contractors", CHEMICAL ENGINEERING AND TECHNOLOGY, vol. 42, no. 1, 14 November 2018 (2018-11-14), pages 196-208, XP055721779, DE ISSN: 0930-7516, DOI: 10.1002/ceat.201800014 the whole document ----- -/--	1-20

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2020/033326

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 565 626 B1 (BAKER RICHARD W [US] ET AL) 20 May 2003 (2003-05-20) see, in particular figures 1,2 and 4 as well as figures 3 and 5-11 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/033326

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6565626	B1	20-05-2003	NONE
